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# Degradation of acrylonitrile-butadiene-styrene and polycarbonate by UV irradiation

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**Abstract**

The effects of ultra-violet irradiation on the microstructure of an oxygen free polymer viz., acrylonitrile-butadiene-styrene and a polymer containing oxygen viz., polycarbonate have been investigated using positron annihilation lifetime measurement. Lifetime results in both polymers in the early stages of irradiation indicate that chain-scission leading to free radical formation is the predominant process. Radiation induced cross-linking becomes dominant in the later stages of irradiation. An interesting feature observed in the present studies is that an oxygen containing polymer attains free volume stability which is attributed as due to the formation of photostabilisers whereas no such stability is observed in the case of an oxygen free polymer. UV absorption spectroscopy results supplement the positron lifetime results that oxygen containing polymer becomes photostabilised. 

*Keywords:* Positron lifetime; Polymer; Free volume; UV degradation; Conformation

## 1. Introduction

Under ambient conditions, polymers are known to undergo degradation, a process which results in the deterioration of polymer properties, characterised by an uncontrolled change in its molecular weight [1]. A polymer can undergo degradation in two stages during its lifetime. One, during its fabrication and the second during its daily usage. The different ways in which the gross properties of polymeric materials are affected by environmental conditions are innumerable. The degradation at molecular level is mainly brought about by energetic agencies and chemical agencies. The energetic agencies can be either thermal or radiant. The radiant energy may be high energy radiation like gamma rays, ion beams, electrons or even low energy radiation like ultra-violet (UV) rays. Some polymers, like poly(methyl methacrylate) (PMMA) undergo chain-scission on exposure to radiation [2] while cross-linking is observed in the case of poly(tetrafluoroethylene) (PTFE) [3] and polyethylene [4]. In certain cases like polycaprolactone, irradiation results in both cross-linking and chain-scission [5]. The exact effect produced in a polymer depends on the structure of the polymer and the nature of radiation [6,7]. Excellent reviews are available dealing with the degradation of polymers [8].

Molecular absorption in the UV-visible region of the spectrum in a polymer is mainly dependent on the chromophores present in its structure. These chromophores are covalently unsaturated groups responsible for electronic absorption. The presence of a substituent group in a chromophore can shift the absorption band to either longer wavelength (bathochromic shift) or to shorter wavelength (hypsochromic shift) [9]. Intermolecular energy exchange occurs by transfer of energy from small chromophore molecules to those on a polymer chains [10]. The energy transfer can also occur by energy hopping from group to group along a polymer chain, exciton bond migration along the backbone of the polymer chains and hopping across loops in the case of folded polymer chains [10].

Energy absorbed in the UV region produces changes in the electronic energy of the polymer molecule resulting from the transitions of valence electrons [9]. The excess energy in the excited state may result in the dissociation of the polymer or may be re-emitted as heat or light [9]. If the re-emitted light is in the visible region of the spectrum, then this will lead to discolouration in the polymer. This is a serious problem in transparent substances like polycarbonate which finds extensive use in the automobile industry for its toughness and transparency. Radiation of wavelength shorter than 350 nm in the UV

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region of the electromagnetic spectrum has sufficient energy to cleave the bonds between the groups in many polymers, thereby producing free radicals. The radicals so produced can initiate further reactions such as cross-linking. This degradation in turn has an effect on the molecular weight of the polymer. Cross-linking leads to an increase in molecular weight while chain-scission has the opposite effect [5]. A change in molecular weight results in a change in viscosity/free volume [11] and a change in free volume in turn results in a change in polymer microstructure.

A literature survey reveals that experimental investigations on the latter issues are sparse. Further, it is interesting to note that the presence of oxygen atoms in a polymer structure has certain roles. Polymers which have aromatic rings and contain oxygen in the form of either ketonic or hydroxy groups are good photostabilizers [12]. In this connection, we found it worthwhile to investigate the microstructural changes in an oxygen-free polymer and in a polymer with oxygen under UV irradiation. For this, we have selected two technologically important polymers viz., acrylonitrile-butadiene-styrene (ABS) which is an oxygen free polymer and polycarbonate (PC) which contains oxygen.

ABS is an economical general purpose polymer used in a wide variety of applications. Sheets of glossy ABS are used in aircraft interior trim, cassette holders, food mixer housings etc. ABS is a copolymer of styrene and acrylonitrile modified with butadiene rubber which acts as a filler [13]. The sample investigated here contains 33% by weight of polybutadiene (PB) and 67% styrene acrylonitrile (SAN). The SAN contains 75% of styrene (St) and 25% acrylonitrile (AN).

The methods of ABS manufacture and studies of the processes affecting the mechanical properties of this polymer have been the subject of a number of articles and reviews [14,15]. However, the UV irradiation induced microstructural changes of this terpolymer have not been studied extensively.

Polycarbonate is another attractive polymer due to its excellent characteristics like impact strength, stiffness, transparency, heat stability and water resistance [16]. Polycarbonate gets its name from the carbonate groups in its backbone chain. The transparency of PC (up to 88% transmittance of visible light) is exploited in such applications as aircraft light housings, aircraft dials, windscreens for cars, safety helmets, contact lenses etc. Panels of PC are used as enclosures for growing plants since it allows diffusion of light and reduces plant sunburn resulting in more production.

Golden and Hazell have studied electron irradiation effects on PC [17]. Torikai et al. [16] have studied photo irradiation effects in PC by combined ESR, viscosity, UV and IR absorption measurements. However, no work has been carried out to understand the detailed microstructural changes in PC upon UV irradiation.

The additional speciality of the ABS/PC combination is that they form blends which find application in computer parts, cassette holders and safety helmets. In this blend, ABS contributes to cost reduction below PC and PC contributes to heat resistance. A very recent study on the effect of Acrylonitrile on PC/ABS blends throws more light on the importance of these two polymers [18].

Various experimental techniques like electron spin resonance [19], mass spectrometry [20], differential scanning calorimetry [21], Viscosity measurement [22], optical absorption measurements and positron annihilation lifetime technique [23,24] have been employed for study of UV irradiation induced changes in polymers. In the present investigation, we have used positron annihilation lifetime (PAL) technique, a well established microanalytical tool to characterize the free volume holes in polymers [25] to understand the UV irradiation induced effects in ABS and PC. Further, UV absorption measurement was also carried out to confirm the formation of new groups due to UV irradiation. The PAL technique is described briefly below.

When an energetic positron from a radioactive source enters a condensed medium like a polymer, it thermalizes by losing its energy in a very short time. It then annihilates with an electron of the medium by a free annihilation process or from a trapped state where the positron is trapped in a defect site and annihilates with an electron of the defect site or forms a bound state called the positronium atom (Ps). Ps can exist in two spin states, a para positronium (p-Ps, particle spins antiparallel) which annihilates with a lifetime of 0.125 ns and ortho positronium (o-Ps, particle spins parallel) which decays with a lifetime of 140 ns in free space. In condensed matter, the lifetime of o-Ps is determined by the probability of electron exchange between itself and the surrounding medium (o-Ps pick-off process). Due to pick-off process, the o-Ps lifetime gets reduced to a few ns. The Ps localizes mainly in the free volume holes of the polymer and as such, the o-Ps lifetime is related to the mean size of the free volume holes [25,26].

## 2. Experimental

ABS and PC having molecular weights of 120,000 and 25,000 respectively were obtained from Goodfellow (Cambridge, England). The UV irradiation was carried out using a 125 W low pressure mercury lamp without any optical filter. The UV lamp was positioned at a distance of 15 cm from the sample. An air flow at a low rate from an electric fan was used to maintain the sample at room temperature during irradiation. The intensity of illumination with this set up was 5555 $Jm^{-2}$ $s^{-1}$. The samples were irradiated for different intervals of time.

Lifetime measurements were performed on these irradiated samples using the PAL spectrometer. For lifetime

measurements, a 15 μCi positron source ($^{22}$Na) was prepared on a pure 0.0127 mm thick kapton foil. This was sandwiched between two identical 15×15 mm samples and used in the lifetime measurement.

The PAL spectrometer consists of a fast-fast coincidence system using KL236 plastic scintillator coupled to a RCA-8575 photomultiplier assembly as detector and has a time resolution of 340 ps. More details of the experimental procedure are reported elsewhere [27,28]. Two to three lifetime spectra each having more than one million counts were collected at each UV irradiation level and consistently reproducible spectra were analyzed into three components with the help of the computer program PATFIT-88. [29] Proper source correction was estimated from a lifetime spectrum of well annealed aluminum using the program RESOLUTION [29]. The UV absorption spectra for untreated and 540 min UV irradiated samples were taken on a HP Model 8452A diode-array UV-visible Spectrophotometer.

## 3. Results and discussion

### 3.1. Positron lifetime results

As in many polymers [30], the three resolved lifetime components are attributed to various states of positron annihilation. The shortest lifetime component $\tau_1$ with intensity $I_1$, is attributed to free annihilation of the positrons with a contribution from the decay of p-Ps. The second lifetime component $\tau_2$ with intensity $I_2$ is considered to be due to the annihilation of positrons trapped at the defects present in the crystalline regions or trapped at the crystalline-amorphous interfaces [31]. The longest lifetime component $\tau_3$ with intensity $I_3$ is attributed to the pick-off annihilation of the o-Ps in the free volume sites present mainly in the amorphous regions of the polymer matrix [30]. It is this third component which is important in understanding the polymer properties through the free volume model and hence the focus of this study.

The annihilation of o-Ps in the free volume cavities is described by a simple quantum mechanical model [32,33] which assumes that o-Ps resides in a simple spherical potential well of radius $R_0$ having an infinite potential. It is further assumed that o-Ps annihilates in a homogeneous electron layer of thickness $\Delta R$ inside the well surrounding the region of the free volume. The final relation according to this model between o-Ps lifetime $\tau_3$, and $R$, the free volume radius is

$$\tau_3^{-1} = 2\left\{1 - \left(\frac{R}{R_0}\right) + 0.159\left[\sin\left(\frac{2\pi R}{R_0}\right)\right]\right\} \quad (1)$$

where $R_0 = R + \Delta R$. The parameter $\Delta R$ was determined by fitting the experimentally measured values of $\tau_3$ in materials of known hole size, such as zeolites. A value of 0.1656 nm was obtained for $\Delta R$. The above relation was used to calculate the free volume hole radius of the polymer samples at each irradiation time. The average size of the free volume holes is then calculated as $V_{f3} = (4/3)\pi R^3$ using the value of $R$ derived from Eq. (1). From the average free volume size, the fractional free volume or the free volume content of the polymer can be calculated as

$$F_v = CV_{f3}I_3 \quad (2)$$

where $C$ is the structural constant. The value of $C$ can be calculated from the thermal expansion coefficient of free volume $\alpha_0$ which is calculated using the value of $V_{f3}$ as

$$\alpha_0 = (V_{f3T} - V_{f3T_o})/V_{f3T_o}(T - T_o) \quad (3)$$

where $V_{f3T_0}$ and $V_{f3T}$ are the free volume sizes at room temperature $(T_0)$ and at a temperature $(T)$ where the free volume expansion is maximum (this was done in a separate isochronal annealing experiment in which the free volume radius and its size were calculated at each annealing temperature. These results are not reported here). The values of $C$ for ABS and PC so obtained are 0.615 and 0.969 nm$^3$ respectively. These values of $C$ were used in the present experiment to calculate $F_v$ with the assumption that $C$ will not change very much upon UV irradiation.

From the results of lifetime analysis, plots of o-Ps pick-off lifetime ($\tau_3$) and hence free volume ($V_{f3}$) as a function of UV exposure time were made and are shown in Fig. 1(a) and (b) for ABS and PC while the corresponding intensity ($I_3$) vs UV exposure time are depicted in Fig. 2(a) and (b) respectively. Fig. 3(a) and (b) presents respectively the variation of fractional free volume ($F_v$) of ABS and PC with UV exposure time.

#### 3.1.1. Free volume changes in ABS

As can be seen from Fig. 1(a), $\tau_3$, and hence $V_{f3}$, rises in the early stages of UV exposure (till 30 min) and then decreases continuously throughout the period of UV exposure. On the other hand, the o-Ps intensity ($I_3$) [Fig. 2(a)] shows the opposite trend with UV exposure time. $I_3$ decreases up to 30 min and then starts increasing throughout the period of UV exposure. The variation of fractional free volume ($F_V$) with UV exposure time is almost the same as that of o-Ps intensity [Fig. 3(a)]. These variations can be explained in the following way.

As described earlier, ABS is a biphasic system having styrene-coacrylonitrile in the continuous phase with a dispersed phase of butadiene derived rubber [13].The possibility of the flexible rubbery butadiene part of ABS being first affected by UV irradiation is more as the $\pi$ electronic chromophore of butadiene absorbs strongly

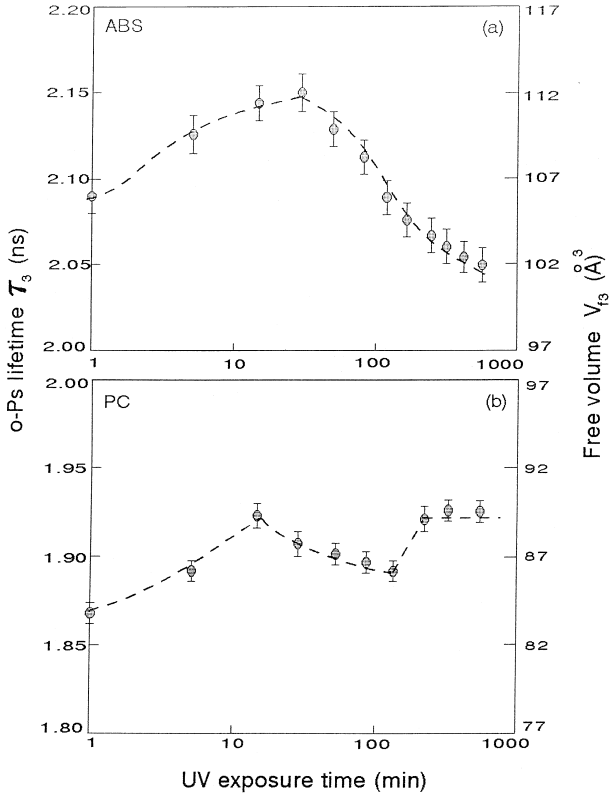


Fig. 1. (a) and (b). Variation of o-Ps lifetime $\tau_3$ and free volume ($V_{f3}$) as a function of UV exposure time. Note dotted lines are to guide the eye.

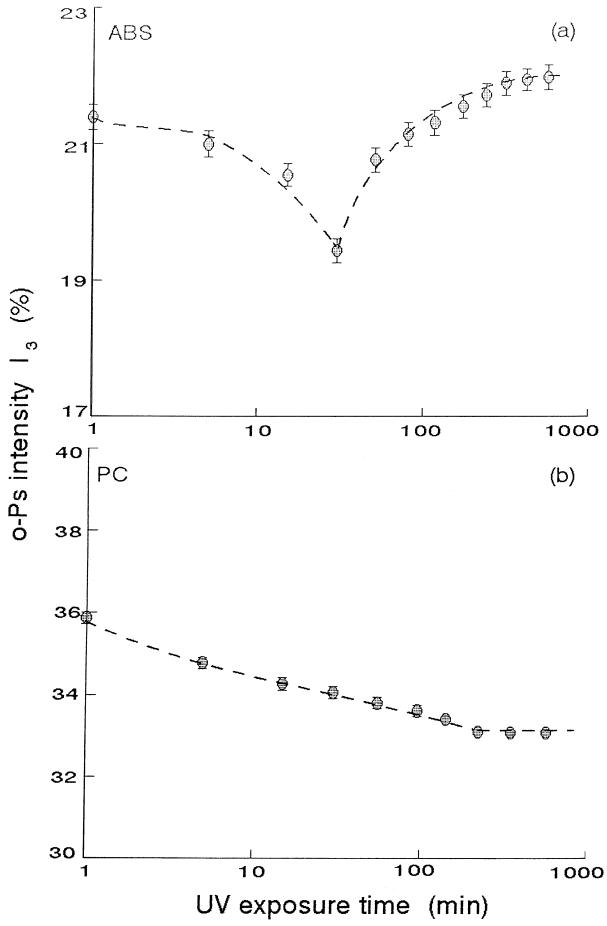


Fig. 2. (a) and (b). Variation of o-Ps intensity ($I_3$) with UV exposure time. Note dotted lines are to guide the eye.

at 217 nm (molar absorptivity at maximum absorption $\varepsilon_{max} = 21{,}000$). According to the empirical method of Fieser and Woodward, the presence of each alkyl or aryl group as substituent in butadiene shifts the absorption by 5 nm to longer wavelength [9]. Thus, in the present case also the presence of substituent groups can result in hypsochromic shift. The branched structure of ABS and the presence of bulky phenyl side groups are expected to result in large sized free volume holes. Intermolecular energy transfer can take place from butadiene part to SAN region of the polymer through the migration of energy along the polymer backbone or due to hopping across the loops in the ABS chain due to its highly folded nature. The SAN part of ABS has two main chromophoric groups. One is the styrene unit which absorbs strongly at 244 nm ($\varepsilon_{max} = 12{,}000$) and also has a weak absorption at 282 nm ($\varepsilon_{max} < 450$). The second is the nitrile group which has a weak absorption at 275 nm ($\varepsilon_{max} < 150$) [9].

It is evident from Fig. 1(a) that there is a considerable effect of UV irradiation on the average size of free volume sites in the ABS matrix. The average free volume size changes from 102 to 112 Å [3] (~9.8% change) upon UV irradiation. It appears that chain-scission leading to free radical production is dominant in the initial stages of UV exposure (till 30 min). Because of the chain-scission, the free volume size increases leading to an increase in the value of $\tau_3$. This is analogous to the result of an earlier study on UV irradiated polymer [22]. Here the authors attribute the decrease in viscosity at the early stages of irradiation to chain-scission and we know that viscosity and free volume are basically interrelated parameters (viscosity is inversely proportional to free volume). Thus, it becomes clear that chain-scission leads to an increase in free volume upon UV exposure.

Photochemical modification of SAN system [34] reveals that the excited styrene molecule reacts with either styrene (St) or acrylonitrile (AN) to form the corresponding diradicals StSt and StAN. It is concluded here that the StSt diradical prefers to cyclise whereas StAN diradical prefers to initiate. This shows that the StAN radical is a comparatively active species. The decrease in $I_3$ could, however, be explained in terms of the spur model of Mogensen [35]. The active free radical StAN may undergo fast reaction with the electrons of the spur and thus reduce the number of electrons available to form positronium. This shows that the free radicals produced by UV irradiation inhibit Ps formation leading to the observed decrease in $I_3$. If Ps formation is

inhibited, it is normally seen as a decrease in o-Ps intensity as observed in earlier studies [26,36]. However, this seems to have little effect on the free volume content as evident from the slight decrease in $F_V$ during the early stages of UV exposure [Fig. 3(a)].

Because of the loosely bound $\pi$ electrons in the side group of SAN regions, cross-linking seems to be more predominant than the chain-scission after 30 min of UV exposure. It is not uncommon for degradation to involve the formation of cross-links between the chains. If this happens at a marked level, the result will be hardening and embrittlement of the material. If the polymer chain hardens, one expects the free volume to decrease. Experimental studies of photo-irradiation of polymers [16,22], reveal that an increase in viscosity is due to cross-linking and hence a decrease in free volume upon cross-linking is justified. Further, another study of UV irradiation on polystyrene also reports cross-linking as the predominant process [21]. It is evident from Fig. 1(a) that there is a decrease in free volume after 30 min of UV exposure. During this process, redistribution of the molecules also takes place leading to an increase in the number of free volume sites and the free volume content. Thus, we observe an increase in the values of $I_3$ and $F_V$ [Figs. 2(a) and 3(a)].

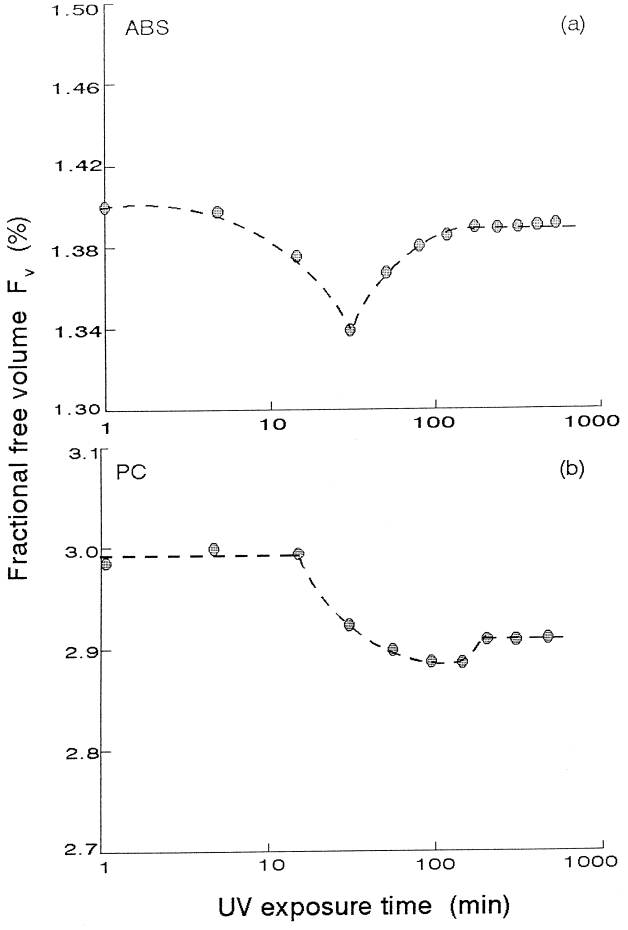


Fig. 3. (a) and (b). Variation of fractional free volume ($F_v$) as a function of UV exposure time. Note dotted lines are to guide the eye.

### 3.1.2. Free volume changes in PC

In the case of PC, $\tau_3$ and $V_{f3}$ increase in the early stages of UV exposure (till 15 min) and thereafter show a slight decrease till 205 min. After this, they show a little increase and finally saturate [Fig. 1(b)]. The $I_3$ decreases slowly from the early stages of UV exposure till 205 min and then remains constant [Fig. 2(b)]. The $F_V$ is almost constant up to 15 min and decreases till 205 min and finally saturates [Fig. 3(b)]. These interesting changes can be explained in the following way.

Polycarbonate contains a carbonyl chromophore which has a weak absorption band resulting from the forbidden transition in the 270–300 nm range ($\varepsilon_{max} < 30$). Further the two benzene chromophores have a weak absorption each at 256 nm ($\varepsilon_{max} = 200$) [9]. As there are no strong chromophores in PC in the wavelength region studied, one can expect less changes in free volume compared to ABS. The average free volume size in PC varies from 83 to 90 Å$^3$ (~8.4% change) under UV irradiation. The initial increase in $\tau_3$ and $V_{f3}$ [Fig. 1(b)] is due to chains-cission mainly at the C–O bonds adjacent to the carbonyl group. An earlier investigation by Zimmermann et al. [37] reports that the C–O bonds adjacent to the carbonyl group in the PC chain are the vulnerable bonds, lacking the resonance stabilisation of the phenyl group. The most important volatile product during PC degradation is $CO_2$ and hence the carbonate linkage is the most reactive group in the polymer [38]. Torikai et al. [16] in a viscosity measurement on UV irradiated PC report the change in molecular weight (Mv) as due to chain-scission and partial cross-linking. Thus, the present variations in the free volume ($V_{f3}$) and its number density ($I_3$) can be interpreted in the light of these results as follows.

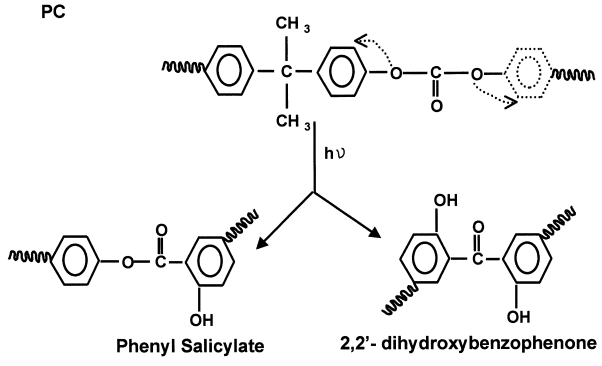


Fig. 4. The mechanism of photo-fries rearrangement in polycarbonate. The benzene ring shown with a dotted line is of the neighbouring monomer.

Initially when chain-scission occurs, the available free volume increases because of the rearrangement of the molecules due to chain-scission similar to the case with ABS. Thus, the increase in $\tau_3$ in the initial stages is essentially due to the increase in the size of the free volume present in the disordered regions. This also indicates that the local electron density near the Ps sites gets reduced.

After 15 min of exposure, there is a slight decrease in the size of the free volume in conformity with the earlier reports, perhaps due to mild cross-linking [16]. As detailed in ABS, in the cross-linked state, the polymer chains are expected to have a closer packing, hence, a reduction in free volume is observed at this stage. The fractional free volume ($F_v$) also starts decreasing from this time of irradiation (after 15 min) as seen from Fig. 3(b).

Fig. 2(b) displays an interesting change in $I_3$ as a function of UV exposure time. It has been reported that photolysis of C–O bonds in PC yields phenyl and phenoxy radicals [39]. The evolution of CO and $CO_2$ which are the by products of phenyl and phenoxy radicals have been observed by mass spectroscopic analysis and the production of phenoxy radicals is five times greater than that of phenyl radicals [39]. These free radicals (mainly phenoxy type) may undergo fast reactions with the electrons of the spur [35] and thus reduce the number of electrons. Thus, similar to ABS, the Ps formation is also inhibited in PC. The observed continuous decrease in the o-Ps intensity till 205 min of UV exposure is an indication of this.

The $\tau_3, V_{f3}$ and $F_v$ show a little raise and level off at the final stages of irradiation. Although the increase is very small, however, it suggests that there is some modification in the polymer. Even $I_3$, which was showing a steady decrease till this point, is constant from here onwards. Most of the aryl esters and carbonates on photolysis undergo a rearrangement called photo-fries rearrangement [10,40,41]. If PC undergoes photo-fries rearrangement upon UV irradiation it will result in the production of photostabilisers, phenyl salicylate (I) and 2,2′-dihydroxybenzophenone (II) [16,42].

Photostabilisers protect polymers from deteriorating effects of light to a considerable extent. They are molecules with aromatic rings having hydroxy and ketonic groups. Phenyl salicylate, 2,4-dihydroxy benzophenone, 2-hydroxy-4-methoxy benzophenone, 2-hydroxy 4-octoxy benzophenone, 2-hydroxy 4-dodecyloxy benzophenone and 2-hydroxy 3,5-dialkyl-benzotriazoles are some typical photostabilizers [12,43]. In all of these photostabilisers, apart from aromatic groups, the presence of oxygen is a common feature. Thus, even though ABS and PC commonly possesses aromatic groups in their structure, only PC contains oxygen. These photostabilisers have an absorption coefficient higher than that of the polymer in the near UV range of the electromagnetic spectrum. The function of a photostabiliser is to absorb the UV radiation and to dissipate the energy absorbed to the environment in some harmless form like heat or radiation of a longer wavelength and thus the photostabilisers act as filters and do allow the radiation energy to attack the polymer molecules [12,43].

The mechanism of photo-fries rearrangement in PC leading to the production of phenyl salicylate (I) and 2,2′-dihydroxybenzophenone (II) is shown in Fig. 4. As discussed earlier, the C–O bond in polycarbonate is more vulnerable (310 kJ/mol) and hence, upon UV irradiation, the oxygen from the weak C–O bond rearranges its position to form a stronger O–H bond (460 kJ/mol) resulting in phenyl salicylate [40]. If the oxygen of the C–O group in phenyl salicylate also undergoes further rearrangement to form strong O–H bond then it results in a more stable 2-2′-dihydroxy benzophenone group. An important point to be noted here is that the products of photo-fries rearrangement are not due to oxidation but are due to the rearrangement of existing oxygen atoms in PC. This kind of stabilisation is achieved without external stabilising agents and is thus the most desirable kind. The classic text by Ranby and Rabek [41] clearly emphasizes the importance of photo-fries rearrangement.

An earlier UV absorption study on UV irradiated PC shows the presence of I and II groups and the authors suggested the possibility of photostabilisation of PC by the rearrangement of the products [16]. If this rearrangement takes place, the existing microstructure of PC may be altered resulting in a slight increase in the lifetime parameters. Although, lifetime or intensity parameters do not identify this rearrangement markedly, the small rise in o-Ps lifetime cannot be totally ignored. The rearrangement in the microstructure results in a small increase in free volume. The increase in o-Ps lifetime on account of chemical modification in a polymer has been reported [44]. This is in agreement with the present proposition that photo-fries rearrangement occurs in PC under UV irradiation. In the case of PC, this rearrangement is possible if and only if the UV irradiation is carried out at a temperature well below its Tg (152°C) [16]. Under the present experimental conditions (the sample was maintained at near room temperature during irradiation), it is possible for this rearrangement to occur leading to the observed free volume stability. Even after prolonged irradiation for nearly 40 h, we found that there was no change in $\tau_3$ and $I_3$ values (Results not shown in graphs) . The constancy of these parameters at higher levels of UV exposure suggests that PC has attained photostability.

### 3.2. UV absorption spectra

To confirm the formation of photostabilised groups in PC, the UV absorption spectra of PC were taken before

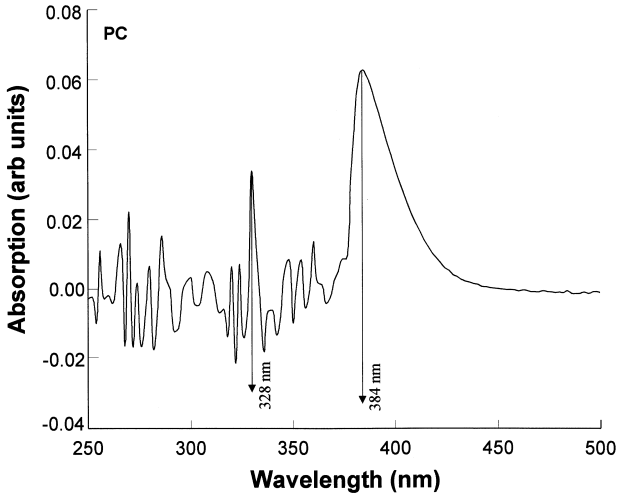


Fig. 5. The difference UV absorption spectrum of untreated and 540 min UV irradiated polycarbonate.

and after UV irradiation and the difference spectrum of the two is shown in Fig. 5. From this figure it is evident that the absorption spectrum shows a strong absorption at 384 nm and a weak absorption at 328 nm which are due to the 2-2′ dihydroxy benzophenone and phenyl salicylate chromophoric groups respectively. These wavelengths of absorption are in close agreement with the values reported in the literature [16,40,45]. The UV absorption spectra show that the rate of benzophenone formation is appreciable even when the competitive absorption by phenyl salicylate is negligible. The difference in the strength of the absorption peaks is due to the fact that most of the oxygen atoms of phenyl salicylate have undergone further rearrangement to form more stable 2-2′ dihydroxy benzophenone.

## 4. Conclusions

Using the PAL technique, we have studied the influence of UV irradiation on the microstructure of ABS and PC and the following observations are made.

- The results seems to indicate that chain-scission leading to free radical formation is the dominant process in the early stages of UV exposure.
- The formed free radicals lead to inhibition of o-Ps.
- Cross-linking occurs after chain-scission in both polymers. Cross-linking is dominant in ABS whilst it is not so in PC.
- The results also show that a polymer containing oxygen attains free volume stability due to photo-fries rearrangement and hence photostability at longer UV exposures whereas no such photo-stability is observed in an oxygen free polymer.
- The present results may be useful in the development of photostabilised PC/ABS blends.

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